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A STUDY OF THE KINETICS OF SEWAGE SLUDGE PYROLYSIS
USING DSC AND TGA

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Abstract

Thermogravimetric and differential scanning calorimetric experiments were performed in nitrogen on four sewage sludge samples at modest heating rates. A mechanism consisting of two independent reactions was derived for an undigested sludge sample. The parameters are: $n_1=10$, $E_1=30$ kcal/g mole, $A_1=1 \times 10^{18}$ sec⁻¹, $n_2=15$, $E_2=60$ kcal/g mole, $A_2=1 \times 10^{25}$ sec⁻¹, with initial weight fractions of $w_1=0.20$, $w_2=0.43$, the remainder being non-reactive ash. Analysis was performed by comparing Friedman multiple heating rate analyses of experimental and model curves in an iterative manner. DSC experiments were used to provide an understanding of the pyrolytic reaction mechanism and heat transfer in the thermogravimetric analyzer. DSC analysis of materials such as sewage sludge was found to be vulnerable to decomposition reactions of small quantities of organic salts in the sample. The suitability of sewage sludge as a feedstock for flash pyrolysis processes is discussed.

Introduction

The natural result of more stringent water quality regulations has been an increase in sewage sludge production from both industrial and municipal sources. At the same time other regulations are reducing the availability of some disposal methods. Expectation of further difficulties has caused many installations, particularly in developed areas, to select on-site disposal methods that avoid renegotiation of disposal contracts at regular intervals. For these reasons, thermal disposal of sewage sludge through either incineration or pyrolysis is becoming attractive despite the obvious technical drawbacks. While sewage sludge does not burn autogeneously, its negative cost could easily outweigh its low fuel value. Any combustion or pyrolysis system that could handle moderate amounts of sludge in addition to its normal feedstock or fuel could find the disposal of sludge profitable.

After a brief discussion of the general fuel properties of sewage sludge and of other work in sludge pyrolysis, this paper presents the results of research on the kinetics of sewage sludge pyrolysis along with some discussion of recent developments in the analysis of non-isothermal thermogravimetric data.

Fuel Characteristics of Sewage Sludge

From the standpoints of both quality and quantities available, sewage sludge does not seem to be a very promising fuel. A 1978 survey of available biomass in New Jersey¹ found that municipal sewage sludge comprised less than 2% of the available biomass in the state, and if gasified would supply an amount of gas equivalent to less than 1% of the state's annual natural gas consumption.

With respect to quality, sewage sludge is even less exciting. Sewage sludge typically leaves a digester or thickener with a solids content of less than 8%.² The use of vacuum filters or filter presses to dewater the sludge to 20-25% solids has been estimated to cost from 40 to 50 \$/tonne depending upon the processes used.³ At this point the sludge will not burn without supplemental energy, usually in the form of large quantities of fuel oil, estimated to average 210 liters/tonne.⁴ Despite these high costs, incineration is often the safest and least expensive way to dispose of sewage sludge. Incineration destroys most of the organic material, leaving only the ash. It should be recognized that the ash itself can be a hazardous waste due to relatively high concentrations of toxic metals. Nevertheless, its reduced volume and biochemical stability often make its disposal less difficult than that of raw or dewatered sludge.

A natural alternative to combustion of sludge using oil as a supplemental fuel is to burn the sludge mixed with municipal solid waste. In this manner, overall moisture content can be reduced enough to permit autogeneous combustion.⁴ Likewise, it would be possible to pyrolyze

such a mixture to produce fuel. Union Carbide has tested the ability of their Purox System to pyrolyze sludge and solid waste mixtures with considerable success.⁵

It is unlikely that a sewage sludge pyrolysis system would be economic merely on the basis of its fuel value. However, many sludge producers are willing to pay as much as \$110/dry tonne for the disposal of liquid sludge. A pyrolysis system would have operating and construction costs similar to those of a sludge combustion system. The added benefit of the salable fuel produced makes sludge pyrolysis seem likely to be profitable.

To provide a frame of reference, proximate analyses were performed on the sewage sludge samples studied in this report. The analyses were performed on a Dupont TGA in a manner that approximates ASTM standards.⁶ Table 1 presents the results with ultimate analyses for similar sludges and both ultimate and proximate analyses for Lignite.

The higher ash content in the digested sludges as compared to undigested sludges is related to the methane production that occurs during anaerobic digestion. The relatively low fixed carbon content of the sewage sludge is a positive factor for gasification applications. The gross heating value of dried sludge is also promising on a dry basis: 1.9×10^7 J/kg (8400 BTU/lb) for raw sludge and 9.7×10^6 J/kg (4200 BTU/lb) for digested sludge.⁷

Table 1

Proximate and Ultimate Analyses of Various Sludges* and Lignite
(% Dry Basis)

Material	Proximate			Ultimate					
	Volatile	Fixed Carbon	Ash	Sulfur	Hydrogen	Carbon	Nitrogen	Oxygen	Chlorine
Stony Brook SB1 (undigested, conditioned sludge)	57.0	9.5	33.5	-	-	-	-	-	-
Stony Brook SB2 (undigested sludge)	53.0	9.7	37.3	-	-	-	-	-	-
Ewing (digested sludge)	42.3	3.1	54.6	-	-	-	-	-	-
Raw Sludge ⁷	-	-	29.1	0.4	5.8	38.9	2.0	23.4	0.3
Digested Sludge ⁷	-	-	55.0	0.8	4.1	24.8	2.7	12.4	0.2
Lignite ⁸ (North Dakota)	44.0	46.7	9.3	1.4	4.4	64.2	0.9	19.6	-

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*The fourth sludge sample (SB3) was omitted from this table due to its unusual origin.

Prior Research

There has been very little research reported on the pyrolysis of sewage sludge, particularly flash pyrolysis. Most studies involve a process that is essentially designed to function as an incinerator with, at best, a waste heat recovery system rather than a fuel production system. These systems often use standard multiple hearth incinerators and simply reduce the available air below that needed for combustion. The product gases are scrubbed and then combusted in a secondary chamber. The purpose of this design is to reduce scrubbing costs by decreasing the volume of air scrubbed.^{9,10}

There have been a limited number of fuel production oriented studies. Union Carbide described pilot plant experiments which used a mixture of sludge and municipal solid waste in their Purox system.⁵ In addition, some research using a batch pyrolysis reactor has been reported by the Bureau of Mines.¹¹ Both studies concluded that the mixture of sludge with municipal solid waste was the most promising way to pyrolyze sewage sludge.

Ongoing research at Princeton is directed toward the development of a flash pyrolysis system using concentrated solar energy to provide the necessary heat for pyrolysis.¹² A detailed understanding of the solid phase pyrolysis kinetics is necessary for the design of such systems, as the reactor throughput is very dependent upon the solid phase pyrolysis kinetics. Consequently, significant efforts have been directed toward a better understanding of the thermal decomposition kinetics of such materials as cellulose, levoglucosan, wood, corncob, cow manure, newsprint

and sewage sludge.¹³

These studies utilize thermogravimetry and differential scanning calorimetry at modest heating rates to develop detailed kinetic models which can then be extrapolated to the higher heating rates that are required for flash pyrolysis. The differential scanning calorimeter has also been found useful for our studies of the energy balance of the reactor.

Experimental Procedures

Sample Selection

To develop a better understanding of the variation among sludges produced by different treatment processes, four sewage sludge samples were tested. These samples were produced by different methods and displayed corresponding characteristics. The samples were collected from two facilities: the Stony Brook Regional Sewerage Authority activated sludge treatment plant and the Ewing Lawrence Sewerage Authority trickling filter with anaerobic digestion plant.

The Stony Brook activated sludge treatment plant combines the solids from the aeration and nitrification stage clarifiers in a thickener. The solids from the thickener are conditioned with lime and ferric chloride and then dewatered using vacuum filters. Three samples were obtained from this facility: (1) after the chemical conditioning and vacuum filtration (SB1), (2) after the thickener but before chemical conditioning and filtration (SB2) and (3) after conditioning and filtration during an experiment in which ash from the sludge incinerator was mixed with the conditioners and the sludge as it was filtered (SB3).

The fourth sample was collected from the Ewing facility. In this facility, the solids from the primary and secondary clarifiers are routed to the anaerobic digestion tanks. After an average residence time of eighteen days, the solids are dried in sludge drying beds. This drying is accomplished only during the warmer months of the year. The sample was obtained from the drying beds after the sludge had completely dried.

The organic fraction of sewage sludge is divisible into two major categories: (1) undigested, settleable organics such as cellulose and (2)

dead bacteria and microbes. These are combined with a large fraction of settleable inorganic materials. The resultant product is very friable when fully dried.

Thermogravimetry

Small (6-7 mg) quantities of each sample were studied in a Dupont 951 Thermogravimetric Analyser (TGA) in flowing nitrogen at nominal heating rates of 1, 2, 5, 10, 20, 50 and 100°C/min. The instrument is a horizontal, null displacement thermobalance. The experimental protocol was based on past experience at Princeton with the same instrument.¹⁴ Briefly, the samples were dried at low temperature, finely ground and stored in a dessicator. The platinum balance pan was charged with a sample and the reactor was purged with nitrogen gas, at atmospheric pressure and approximately 100 ml/min flow rate. Orientation of the thermocouple and sample pan were held constant with respect to each other and the furnace. The samples were dried at 100°C and then heated at a nominally linear heating rate from 110 to 600°C. During each run an independent check was made of the heating rate, as the actual heating rate was generally higher than that indicated on the instrument. The fumes produced by pyrolyzing sludge are extremely offensive and care had to be taken to vent them properly.

The calibration of the thermocouple was checked periodically, using melting point standards, throughout the months in which the experiments were performed. In addition, occasional experiments with pure cellulose helped verify the reproducibility of the instrumental and procedural variables.

As described by Antal, Friedman and Rogers,¹⁴ the location of the thermocouple with respect to the sample strongly affects the reported temperature. Additional experiments were performed in the TGA with a second thermocouple directly in contact with either the empty pan or a cellulose sample in the pan. The thermocouple supplied with the TGA was held in its customary position: 2-3 mm outside of the pan at mid-section. The second thermocouple prevented precise weight measurement during the experiments; consequently this method cannot be used with a DuPont TGA for anything but study of the heat transfer to the sample during pyrolysis.

It was found that the sample temperature was significantly less than that reported by the conventional thermocouple. The magnitude of this difference varied with the heating rate. The effect can be attributed to two sources: (1) the specific heat of the pan, quartz support beam and the sample and (2) the heat of reaction of the sample. The temperature differences before and after pyrolysis and in the empty pan experiments can be attributed to the specific heats. The magnitude of the difference varied from about 8°C at a heating rate of 2°C/min to 20°C at 100°C/min and was independent of the mass of the sample in the pan. Consequently, the specific heat of the sample does not appear to be significant in comparison to that of the pan. This is to be expected since the mass of the pan is approximately 16 times that of the average sample. The heat of reaction of the sample is, however, relatively significant, causing an additional temperature difference of 2°C at 2°C/min to 10°C at 100°C/min.

The second thermocouple prevented installation of the fume vent tube

so these experiments were not performed with sewage sludge. However, as will be discussed later, this effect has been included in the numerical simulations of the experimental data. The effect of these temperature differences appears as spreading of the weight loss curves with heating rate beyond that which would be predicted by kinetic theory alone.

Sewage sludge is clearly a heterogeneous material and significant variability in sample composition can be expected. As seen in Figures 1 and 2, the decomposition curves exhibit anomalous crossings, particularly at higher temperatures. These anomalous crossings did not reproduce experimentally. This irregularity is doubtlessly due to variability in the sample composition as experiments with pure substances such as cellulose did not show such variation.¹⁴ As is expected in thermogravimetric experiments, the variation for the sludges was most prominent at lower weight fractions. At weight fractions above 0.8 the curves were fairly repeatable, particularly for the SB2 sample (Figure 1). Consequently, in our later analysis we attached the greatest importance to the data above a weight fraction of 0.8.

Figure 3 presents a 10°C/min thermogravimetric (TG) curve for each of the samples studied. All samples exhibited similar behavior although the final weights varied considerably.

Differential Scanning Calorimetry

To provide further insight into the reaction kinetics in addition to data needed for heat transfer studies of the TGA and the flash pyrolysis reactor, a series of sewage sludge experiments were performed on a Setaram Differential Scanning Calorimeter (DSC). The design of the instrument is quite different from most DSC's. The calorimeter consists of two ceramic tubes with an I.D. of about 7 mm, which can be oriented either horizontally or vertically. These tubes are encased in a thermopile which is surrounded by a furnace. The entire assembly is encased

in a water cooled jacket. A small boat, about 1 cm long and the diameter of the tube, can be slid from either end of the tube into the active region. For the sewage sludge experiments the calorimeter head was operated in the horizontal position using an open ceramic boat. A seeping gas flow of 4-5 ml/min of nitrogen was used to maintain an inert environment.

It was found that the calorimeter is very sensitive in its design range but does not yield reproducible data at heating rates above 20°C/min. Setaram provides a calibration curve with the DSC cell. This curve was checked using a Joule effect calibration device, a melting point standard (zinc), and the crystal phase transition enthalpy change for quartz. In all cases, the calibration curve and the calibration experiments correlated well.

The instrument was very sensitive to changes in the specific heat of the materials in the sample and reference zones, most notably that of the ceramic boats. Each sample and reference boat combination exhibited a baseline that was unique, not only in its offset but also in its curvature. This baseline was further influenced by the specific heat of the ash and fixed carbon remaining at the end of each run. To eliminate these effects, a baseline experiment was performed on the ash and char after each pyrolysis run. This baseline was then subtracted, using the computer, from the sample curve. The resultant curve approximates the specific heat of the volatile materials that have not yet volatilized in addition to the energy consumed by the chemical reactions. All DSC curves presented in this report were derived in this manner.

All of the samples were studied from 110°C to 600°C at a heating rate of 10°C/min and two of the samples were also studied at 2° and 5°C/min. The sample sizes ranged from 35 to 40 mg, before final drying in the calorimeter. Figure 4 presents the 10°C/min experiments for all four samples. The curves for the two samples containing conditioners exhibit more peaks than the other two: these peaks are due to decomposition of salts produced by the conditioners, lime and ferric chloride. These large surplus endotherms represent a significant amount of energy. Designers of sludge combustion and pyrolysis systems must carefully weigh the filtration benefits provided by the conditioners versus the heat they consume in a combustor or pyrolysis reactor.

Figures 5 and 6 present TG, DTG and DSC curves for the two unconditioned sludges at heating rates of 10°C/min. Both samples exhibit very large endotherms before significant weight loss occurs. The meaning of this endotherm, apart from its heat requirements, has not been determined. It is significant that the reaction producing weight loss requires very little energy. In future studies, it would be interesting to determine the cause of this large endotherm. If it is an initiation reaction that the weight loss reactions depend upon, it should be included in the kinetics. If instead, it is due to another material and the reaction produces no fuel, it would be worthwhile to attempt to remove the material from the sludge before pyrolysis. Determination of the cause of this endotherm is beyond the capabilities of conventional TG and DSC; consequently we were unable to discover what process caused the peak. However, as will be discussed later, it does not appear to affect the kinetics.

Overview of Solid Phase Pyrolysis Kinetics

Solid phase thermal decomposition is conventionally described by the following rate law:^{15,16,17}

$$\text{rate of conversion} = dc/dt = k(T) f(c) \quad (1)$$

$$c = (w - w_i) / (w_i - w_f) \quad (2)$$

$$k(T) = A \exp(-E/RT) \quad (3)$$

where w is the time dependent sample weight, w_i the initial sample weight, w_f the final weight, A the pre-exponential factor, E the activation energy, R the universal gas constant and T the time dependent absolute temperature. The choice of $f(c)$ is less well defined, and is believed to be very dependent upon the particular decomposition mechanism. A considerable number of applicable functions have been proposed for the range of possible rate controlling mechanisms.^{18,19} The most commonly used function is:

$$f(c) = (1 - c)^n \quad (4)$$

where n is the order of the reaction. This function has been used with considerable success in modeling the pyrolysis of cellulose, wood chips, paper and cow manure in steam and nitrogen.¹⁴

The energy consumption or enthalpy change as a result of the reactions is in theory governed by the same kinetics that control the weight loss. The major difference is that the heat of reaction and specific heat of the sample must now be considered. The output from the DSC for

a single reaction can be described by the equation:

$$\text{DSC signal} = (w_s C_{ps} + w_c C_{pc}) dT/dt + w_i \Delta H A \exp(-E/RT) (1-c)^n \quad (5)$$

where w_s is the weight of unreacted sample, w_c the weight of char products, C_{ps} and C_{pc} the specific heats for w_s and w_c respectively, dT/dt the heating rate, $w_i \Delta H$ the heat of reaction for the sample.

Many substances, including sewage sludge, decompose by more than one reaction, consequently, it is important to understand the effect that multiple reactions will have on the weight loss curves. For a system of two simple reactions, there are basically three possible combinations: independent, consecutive and competitive reactions, all of which have been studied.^{19,20,21,22}

A myriad of curve shapes can arise from these three combinations, depending primarily on the relative magnitudes of the kinetic parameters of the two reactions. The problem becomes considerably more complex once a third or fourth reaction is considered. To isolate the overall mechanism from the other possibilities, it is necessary to observe the reaction under a broad range of temperatures or heating rates, using isothermal or non-isothermal experiments, respectively. Considerable success has been reported in the study of cellulose decomposition, which has been described as a combination of an initiation reaction followed by two competitive reactions.^{23,24}

Although a single, individual derivative peak does not necessarily indicate the presence of only one reaction, two derivative peaks are evidence of at least two reactions.

The DSC curves represent a derivative signal and consequently provide information similar to that of the derivative thermogravimetric (DTG) curves. Aside from the broad initial peak, figure 5 demonstrates excellent agreement between the DSC and DTG curves for the SB2 unconditioned undigested sludge. Figure 6 presents a less easily interpreted picture for the Ewing sludge sample, as there is no endotherm evident where the DTG peak occurs. This is evidence that the weight loss reaction for the digested sludge is close to autothermic. The height of the corresponding peak for the SB2 undigested sludge supports this hypothesis.

Kinetic Interpretation of Experimental Data

It is too mathematically cumbersome to develop methods for the kinetic analysis of experimental data which are keyed to each potential pyrolysis mechanism. A more expedient approach is to choose a method for the analysis of experimental data that assumes a single reaction, and to study how this method responds to different mechanisms. The method described in this paper is the Friedman multiple heating rate method¹⁶ for determining the activation energy, and a logical extension of the method for determining the order. The methods are derived by combining equations 1 and 3 and taking the natural logarithm to obtain:

$$\ln dC/dt = \ln A - E/RT + n \ln (1-c) \quad (6)$$

If c is held constant and $\ln dC/dt$ is plotted vs $1/T$, the resulting slope is $-E/R$. Likewise, if T is held constant and $\ln dC/dt$ is plotted vs $(1-c)$ the slope is n .

Since both methods study the progress of the reaction at a particular temperature or degree of conversion, they are able to follow the reaction through periods of dominance by different steps in the overall mechanism.

A FORTRAN program was developed to perform the analysis. To improve our understanding of how the Friedman method responds to different mechanisms, a catalog of synthetic decomposition curves covering the range of possible mechanisms was developed using another FORTRAN program which employs a Runge-Kutta algorithm for the integration of the pyrolysis rate equations. These simulated curves were then analyzed using the Friedman

analysis program which produces a plot of activation energy versus conversion.

It was learned that the Friedman method can indeed detect transitions from one reaction to another. In general, it can be said to present an average activation energy at each point, based on the degree to which each reaction contributes to the weight loss. The manner in which this average or apparent activation energy changes with conversion and heating rate is relatively unique for a given mechanism.²⁵

Similar results were obtained using the analogous method for determining the order. In many cases, the apparent order reported was essentially an average similar to the results with the activation energy. However, in other cases the apparent order was higher than any of the orders for the reactions that comprised the mechanism. This peculiar behavior is not fully understood and will receive more study.

Despite all its strengths, the Friedman method is not able to separate all reactions. If the kinetic parameters are very similar, the Friedman method will seem to report only one reaction. In such cases, it makes little difference from an engineering standpoint whether there really are one or two reactions since the behavior is the same as if there were only one.

The rate equation integration program was further extended to consider the rate of heat transfer to the sample in the TGA. In this manner curves were constructed to simulate the way the hypothetical material would decompose in the DuPont TGA rather than in an ideal furnace. This heat transfer step was based on the TGA experiments with an additional

thermocouple and upon the DSC experiments. For reasons that have yet to be determined, the sewage sludge appeared much less influenced by heat transfer than previous experience with powdered cellulose. Consequently, the heat transfer step was removed from the program when models were generated for the sewage sludge as it added significantly to the computing time.

Figure 7 presents the Friedman activation energy curves for the SB2 unconditioned undigested sludge. The two curves reflect a Friedman Analysis of low heating rate (1-10°C/min) data, and high heating rate (10-100°C/min) data. The transition from an apparent activation energy of approximately 20 kcal/g mole to approximately 50 kcal/g mole is known from earlier work²⁵ to be the signature of parallel reactions. This signature also indicates that it is unlikely that an initiation reaction exists as might be interpreted from the DSC curves. Due to time and financial limitations, modeling efforts were restricted to the SB2 unconditioned, undigested sludge, since of the sludges studied, it is the most suitable pyrolysis feedstock.

The choice of a parallel reaction model is supported by the composition of the sludges studied. As mentioned earlier, the organic fraction of the sludges is primarily dead bacteria, and settled organics (presumably composed of cellulosic materials). These two components would be expected to decompose by separate or parallel reactions with considerably different kinetic parameters.

The large difference between the activation energies reported for the two separate reactions in the Friedman curves indicates that the re-

actions occur in different temperature ranges. This behavior was used to determine the relative quantities of the two materials in the sample. Isothermal experiments were performed at 200, 250 and 300°C. The most useful experiment was the one performed at 200°C. At this temperature, the reaction rate of the low activation energy reaction was at least two orders of magnitude greater than that of the higher activation energy reaction. After an initial period of rapid weight loss, the rate of reaction quickly became negligible. This initial weight loss was assumed to be due to the low activation energy reaction.

It was not possible to determine experimentally the fraction of the char that was produced by each reaction: however, since the total char was known from the proximate analysis (Table 1), it was possible to develop an algebraic relationship between the char production of each reaction and the initial masses of the reactants. This relationship had only one free variable which was taken to be the initial mass fraction of the low activation energy reaction.

Combining the information from the Friedman analyses with the relationship derived for the initial masses and the char production, a trial model was prepared using the rate equation integration program discussed earlier. This model was analyzed with the Friedman program and the results, along with the simulated TG and DTG curves, were compared to the experimental data. This process was repeated iteratively approximately 35 times until an acceptable model was developed. Table 2 presents the final model parameters and Figures 8 and 9 are the simulated TG and DTG curves (respectively) for the model using the heating rates

studied. To provide a representative example of the quality of the model, Figure 10 presents a model TG curve with an experimental TG curve for the same heating rate. The previously mentioned variability in the sample composition causes the expected error at weight fractions below 0.8 to be so high that the fit is as good as could be expected. In fact the fit was based more on the behavior of all the curves together than on a curve for a single heating rate. Figure 11 presents Friedman activation energy curves at high and low heating rates for the model. Comparison with Figure 7 shows that the model has a Friedman curve similar to the experimental data, particularly for weight fractions above 0.8. It is important to note that the heterogeneous nature of the sludge prevents determination of much more than an empirical model for its thermal decomposition. The inability to exactly reproduce experimentally the decomposition curves also considerably relaxes the error requirement for the mechanism.

The difficulty in developing a model that fits the experimental data is, in part, a justification of the uniqueness of the model. We feel confident in asserting that there is no significantly different combination of parameters for two parallel reactions that would also successfully fit the experimental data. The possibility of a totally different mechanism does exist but it is unlikely that any one reaction mechanism would reproduce the data.

The high apparent order is unusual. Orders of 15 are far beyond what is theoretically justified in gas phase kinetics, from which by analogy, solid phase kinetics are drawn. As these high orders are necessary to obtain a satisfactory fit, either the mechanism is incorrect or there is need to develop a better theory for solid phase pyroly-

Table 2

Kinetic Parameters for Model of the SB2 Unconditioned Undigested Sludge

	Reaction 1	Reaction 2
A (sec ⁻¹)	1×10^{18}	1×10^{25}
E (kcal/g mole)	30.	60.
n	10.	15.
Stoichiometric Factor	0.480	0
Initial Fraction	.202	.425

Where stoichiometric factor = $\frac{\text{fraction of solid product}}{\text{fraction of solid reactant}}$

sis. It is not unlikely that the manner in which molecules interact in the solid phase during pyrolysis, potentially involving many individual molecules, is very different from gas phase interactions.

Conclusions

The combination of DSC, TG and DTG data provides a wealth of information for kinetic analysis of the thermal decomposition of solid materials. This combination is particularly useful when a complex reaction mechanism is suspected. Friedman analysis proved to be a particularly useful method for determining complex reaction mechanisms. Unfortunately these methods alone did not provide enough information to precisely choose a mechanism and its parameters. Iteration with a FORTRAN program that solved the rate equations was necessary to obtain a close fit to the experimental data.

Although variability in sample composition makes kinetic analysis of sewage sludge difficult, there is strong evidence that it decomposes by two high order parallel reactions.

Chemical conditioners used as dewatering agents significantly increase the quantity of energy required to achieve pyrolysis.

Despite its high ash and water content, sewage sludge could prove to be a profitable pyrolysis feedstock if mixed with municipal solid waste. Its negative cost, high volatile content and its friability contribute to its attractiveness as a feedstock for flash pyrolysis processes.

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Figure Titles

- Figure 1. Weight loss curves for the Stony Brook SB2 undigested sludge
(— — — 1.0, — — — 2.0, — — — 5.1, — — — 10.3,
--- 20.8, — — — 55.4°C/min)
- Figure 2. Weight loss curves for the Ewing Digested sludge
(— — — 1.9, — — — 5.7, — — — 10.5, — — — 20.4,
--- 54.1, — — — 115.6 °C/min)
- Figure 3. A comparison of weight loss curves at 10°C/min for the four
sludge samples studied
(— Ewing, — — — SB1, — — — SB2, — — — SB3)
- Figure 4. A comparison of DSC curves at 10°C/min for the four sludge
samples studied
(— Ewing, — — — SB1, — — — SB2, — — — SB3)
- Figure 5. TG, DTG and DSC curves for the Stony Brook SB2 unconditioned
sludge at 10°C/min
(— TG, — — — DTG (indicated scale $\times 2.07 \times 10^{-3} \text{ sec}^{-1}$),
— — — DSC (indicated scale $\times 12.3 - 3.1 \text{ mW}$))
- Figure 6. TG, DTG and DSC curves for the Ewing unconditioned sludge
at 10°C/min
(— TG, — — — DTG (indicated scale $\times 1.45 \times 10^{-3} \text{ sec}^{-1}$),
— — — DSC (indicated scale $\times 12.81 + 3.85 \text{ mW}$))
- Figure 7. Friedman activation energy curves at low and high heating
rates for the SB2 unconditioned sludge
(□ 1.0, 2.0, and 5.1° C/min; ■ 10.3, 20.8, and 55.4° C/min)
- Figure 8. Simulated TG curves for the SB2 unconditioned, undigested
Stony Brook sludge
(— — — 1.0, — — — 2.0, — — — 5.1, — — — 10.3,
--- 20.8, — — — 55.4°C/min)
- Figure 9. Simulated DTG curves for the SB2 unconditioned, undigested
sludge
(— — — 1.0, — — — 2.0, — — — 5.1, — — — 10.3,
--- 20.8, — — — 55.4°C/min)
- Figure 10. A comparison of the simulated TG curve with the experimental
TG curve at 10°C/min
(— — — experimental data; — — — kinetic model)
- Figure 11. Friedman activation energy curves at low and high heating
rates using the simulated TG data
(□ 1.0, 2.0, 5.1°C/min; ■ 10.3, 20.8, 55.4°C/min)

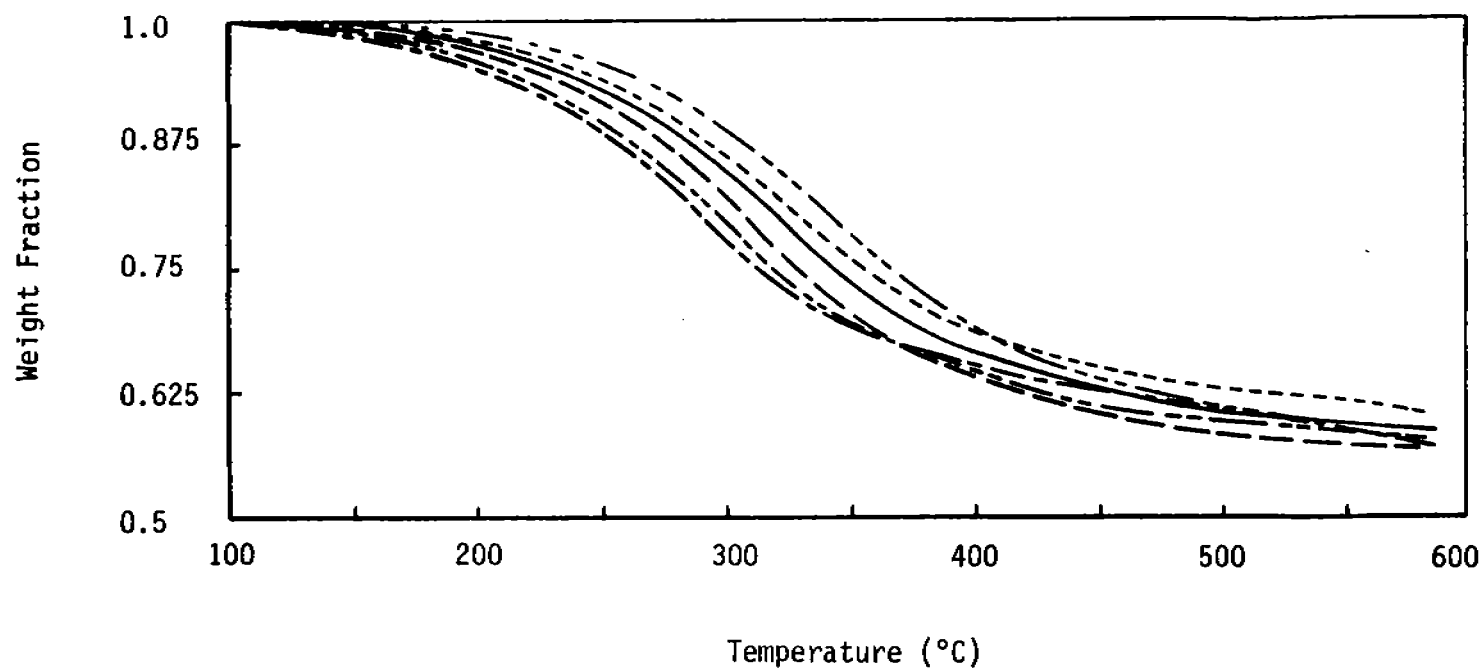


Figure 1

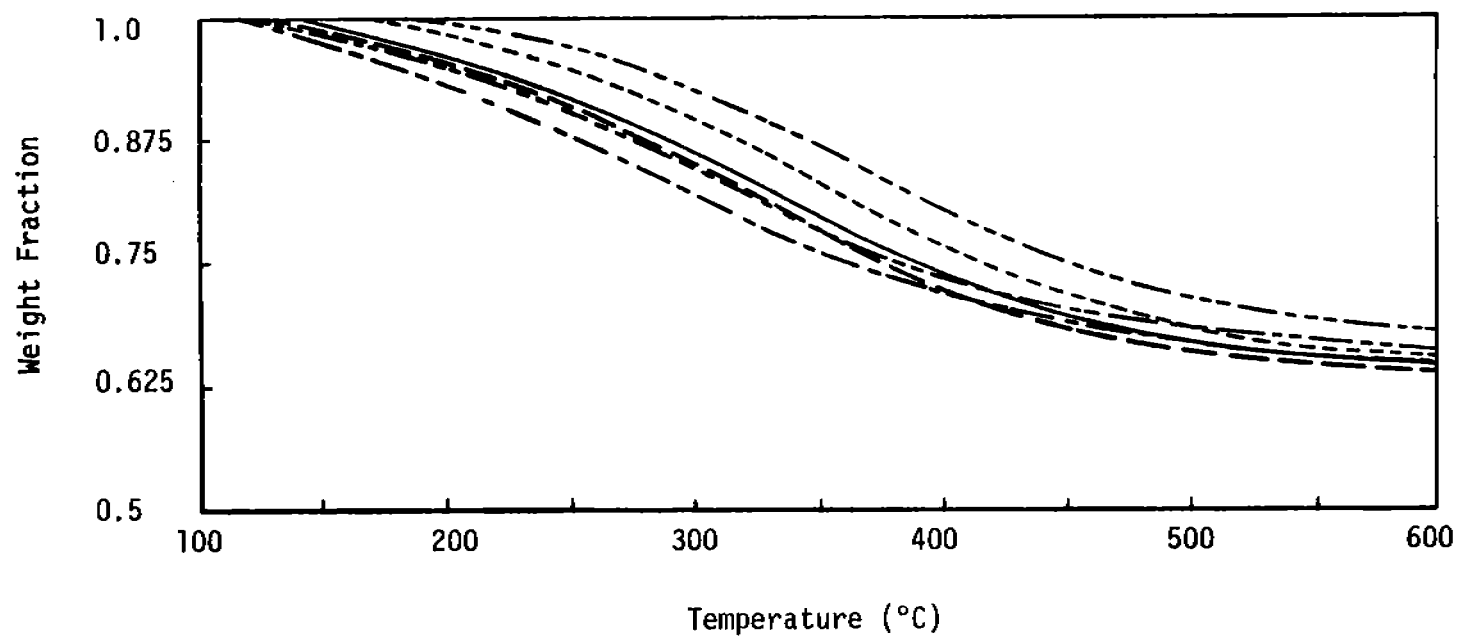


Figure 2

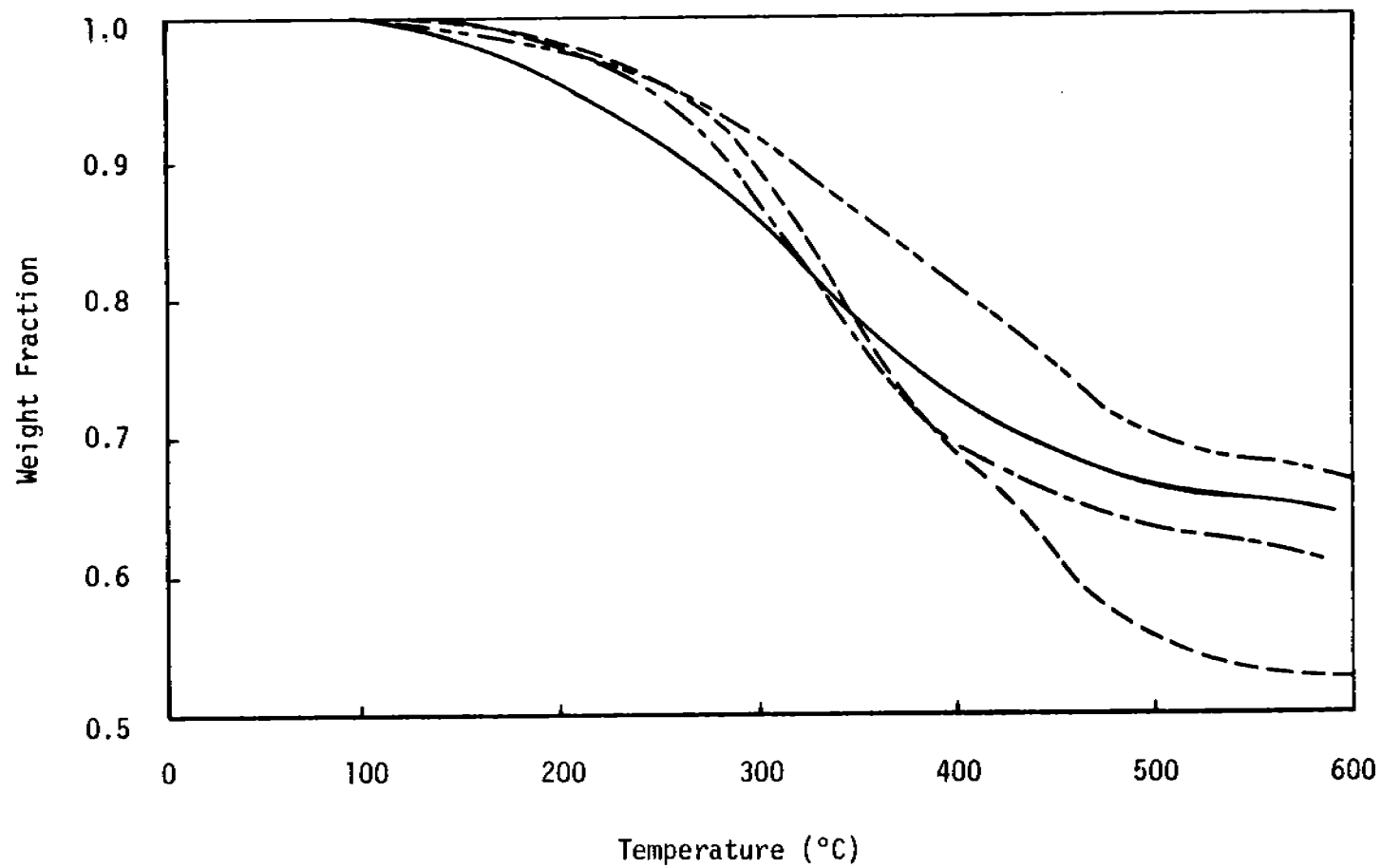


Figure 3

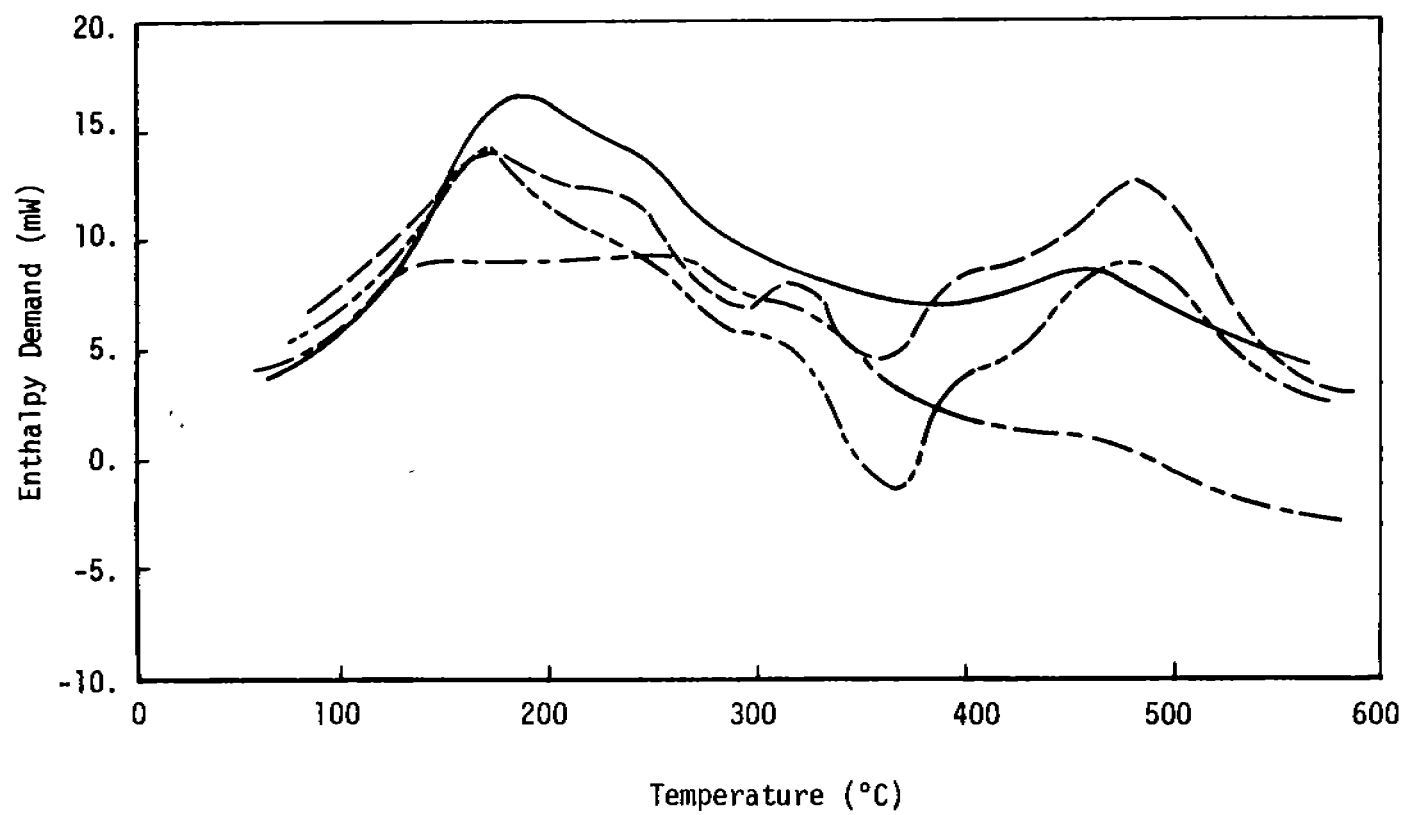


Figure 4

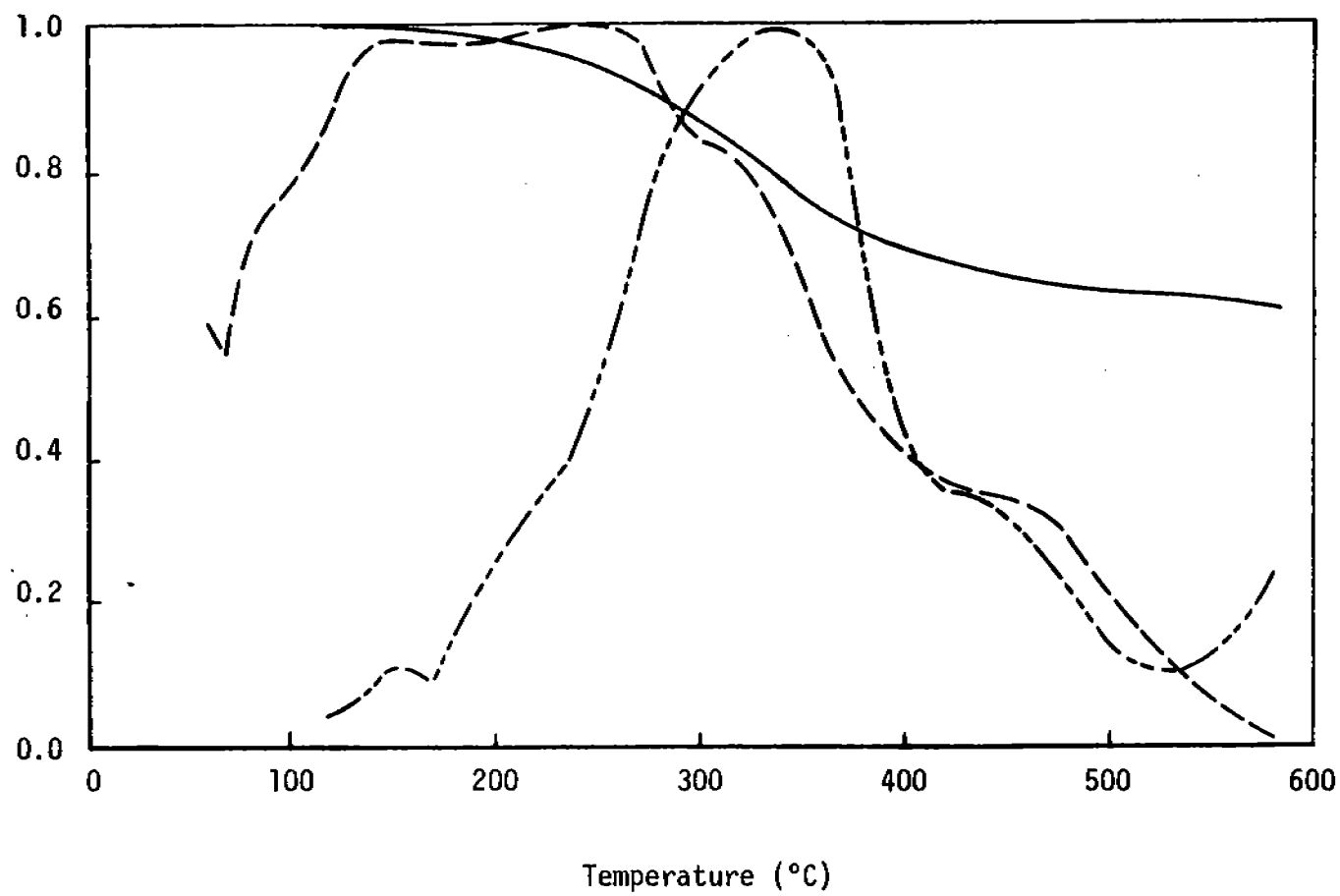


Figure 5

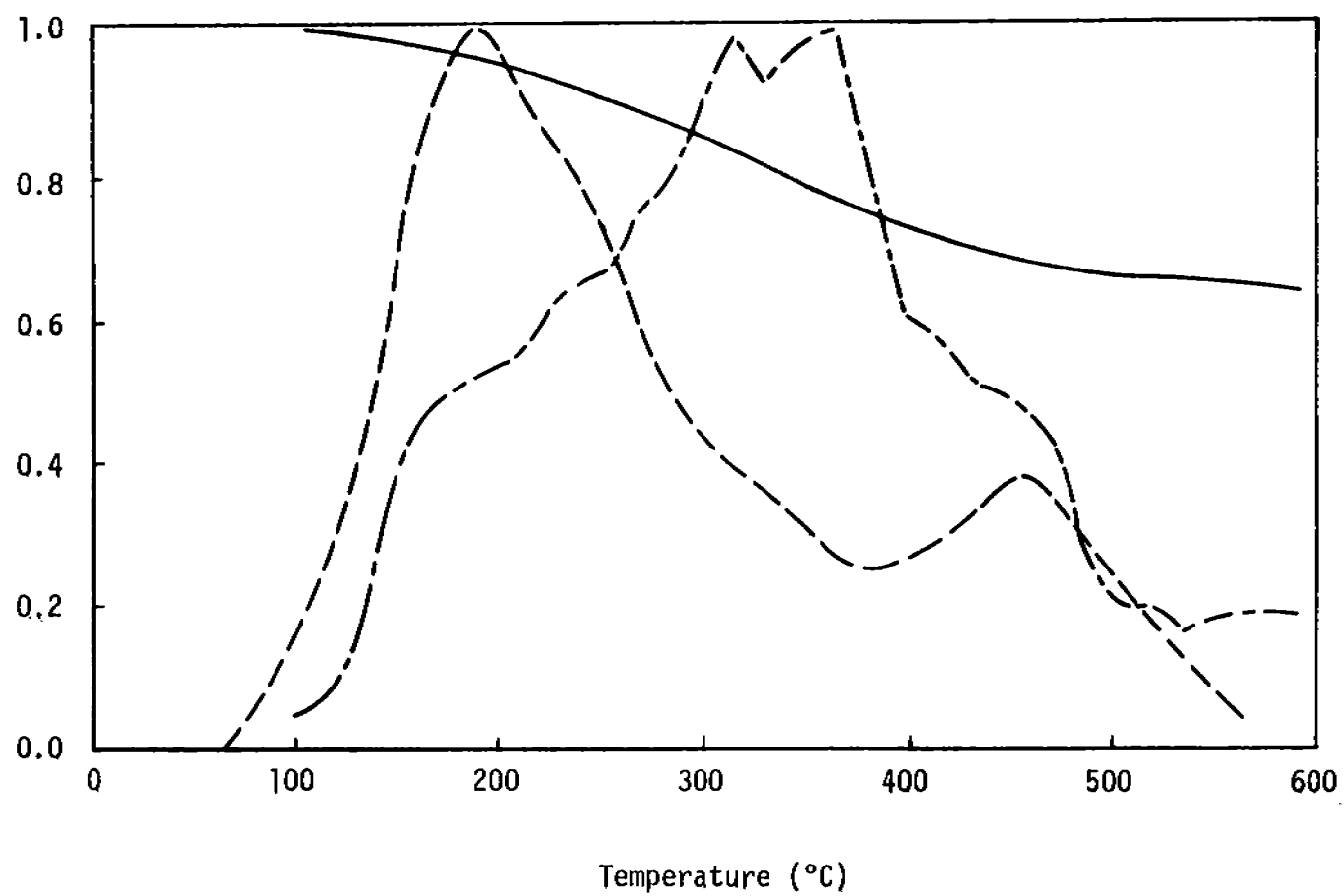


Figure 6

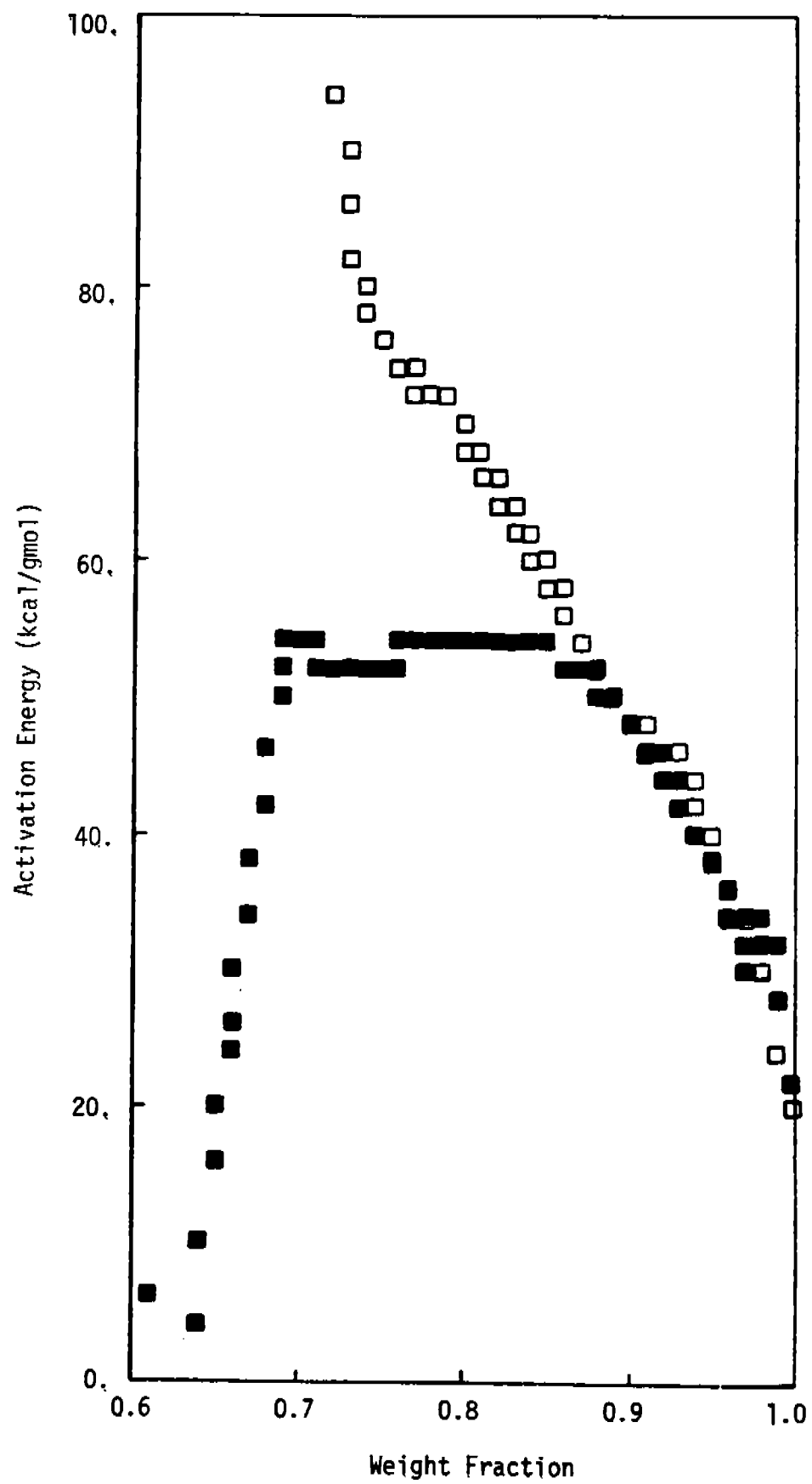


Figure 7

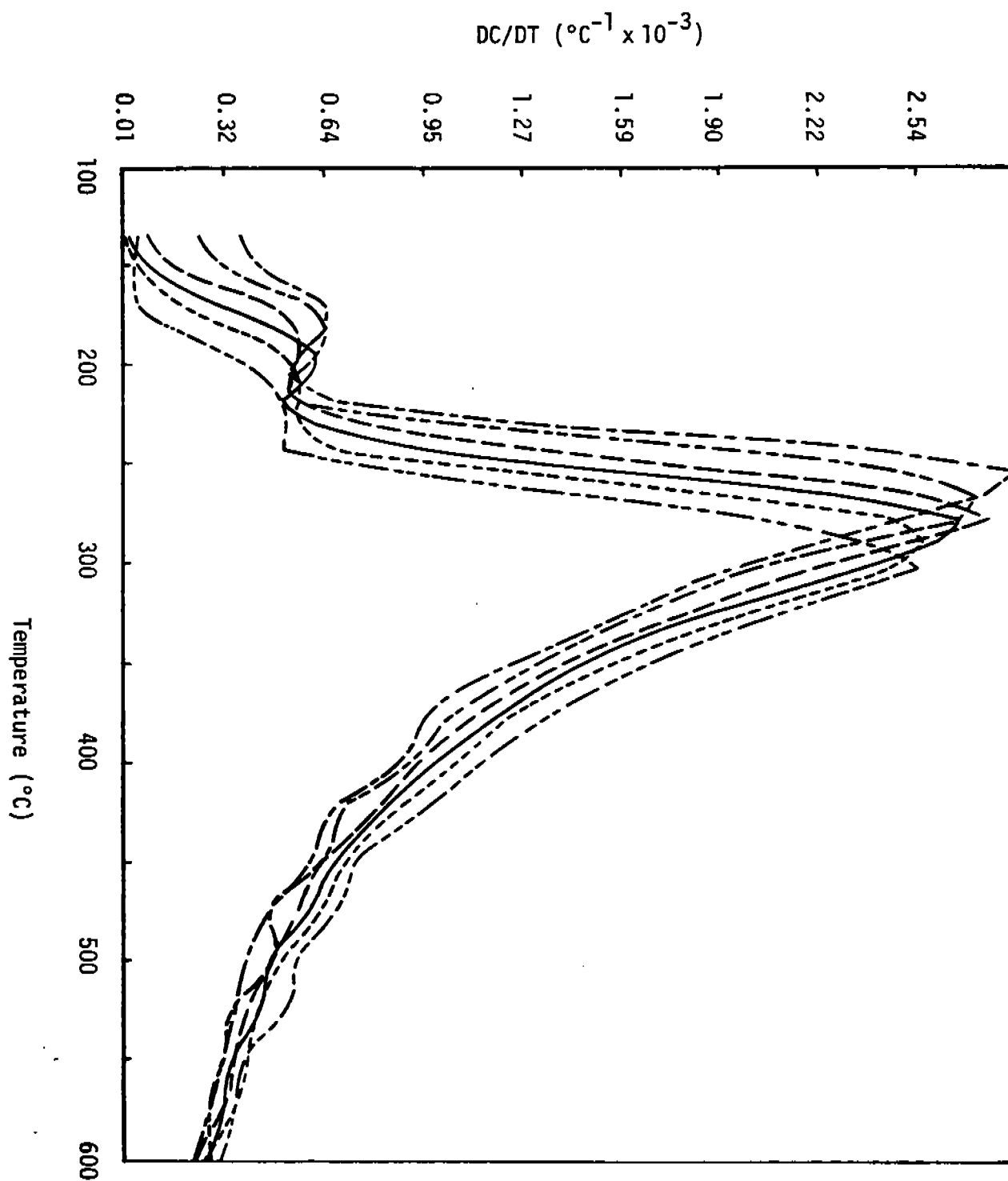


Figure 9

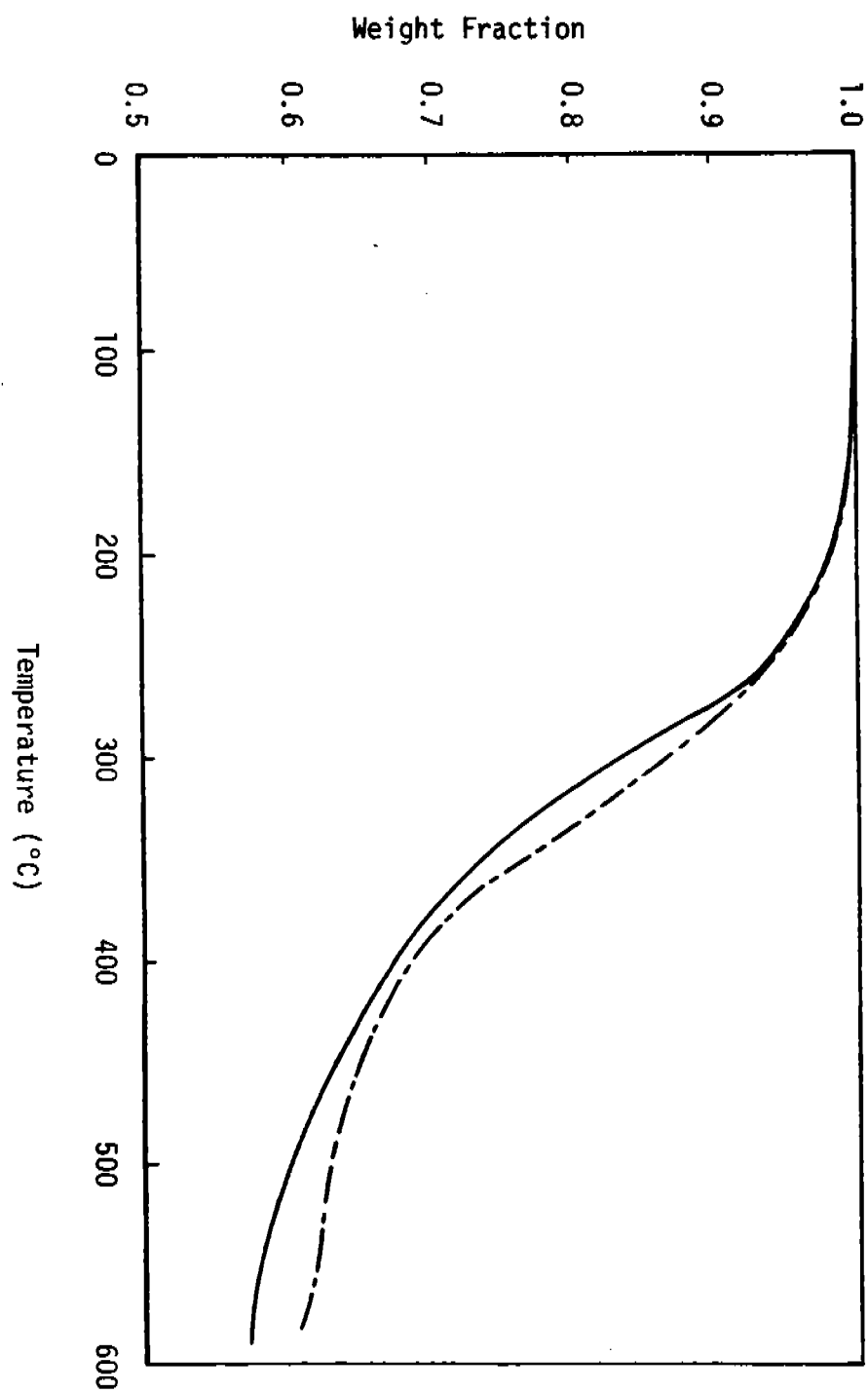


Figure 10

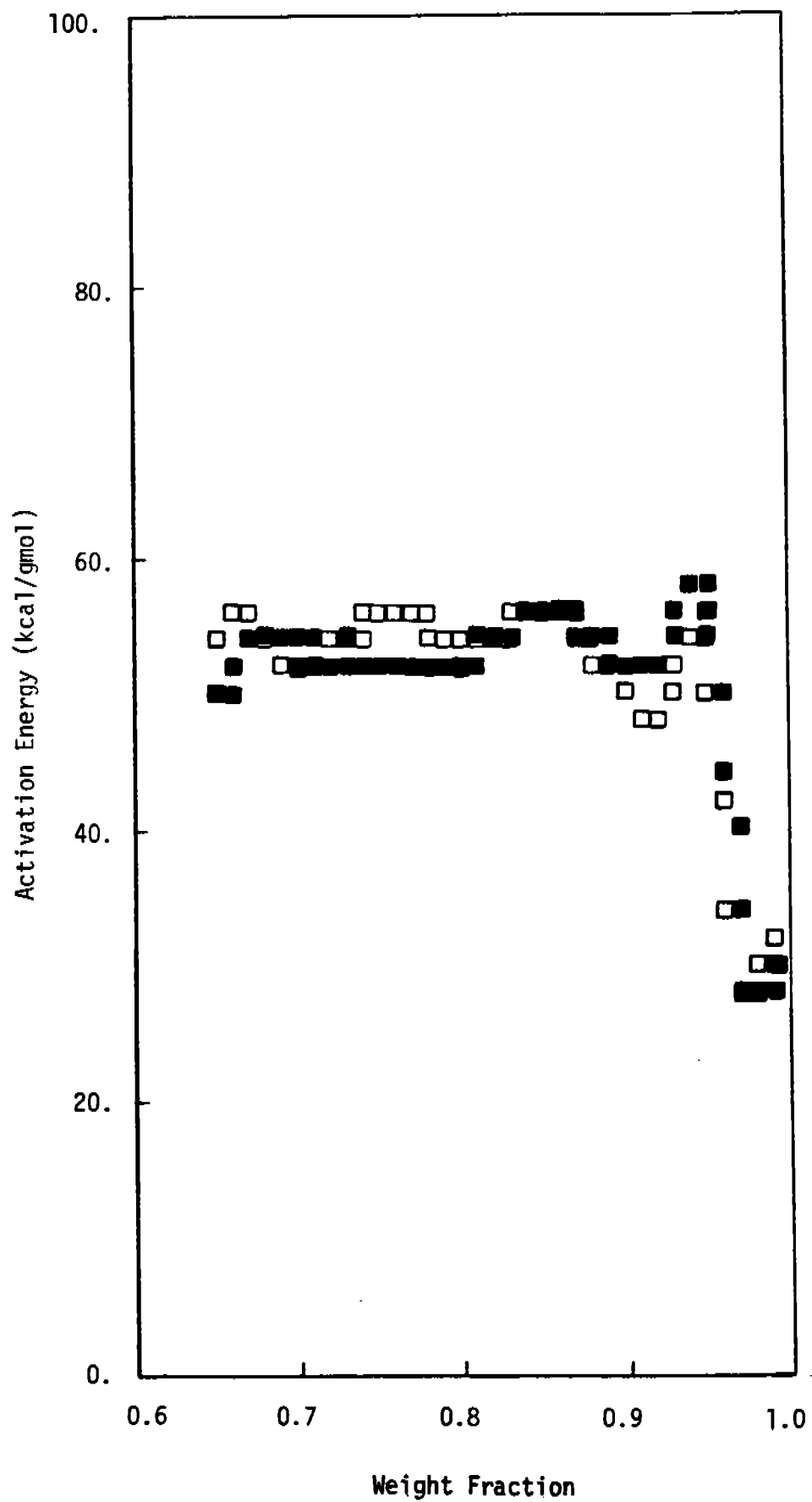


Figure 11